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치의학박사 학위논문

Bonding to Dental Zirconia Ceramic

I. Comparison of shear test methods to zirconia

II. Shear bond strength of multi-purpose, universal adhesives to zirconia

치과용 지르코니아 세라믹에 대한 접착

I. 지르코니아에 대한 전단접착강도 시험방법의 비교

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Abstract

Bonding to Dental Zirconia Ceramic

I. Comparison of shear test methods to zirconia

II. Shear bond strength of multi-purpose, universal adhesives to zirconia

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Introduction

The first purpose of this study was to determine the bond strength of resin cement to zirconia ceramic after different surface treatments by means of three shear bond strength (SBS) test methods and to compare the sensitivity and the reliability of the SBS test methods. The second purpose was to evaluate the performance of the new universal adhesives (Single Bond Universal, 3M ESPE and All-Bond Universal, Bisco Inc.) as a

surface treatment agent for zirconia with a test method established through the foregoing experiment.

Materials and methods

In Experiment I, polished zirconia ceramic (Cercon[®] base, DeguDent) slabs were randomly divided into four surface treatment groups: no treatment (C), airborne-particle abrasion (A), treatment with a conventional phosphate monomer-containing primer (Alloy Primer, Kuraray Co.) (P), and treatment with Alloy Primer after airborne-particle abrasion (AP). Bond strengths of resin cement to the zirconia specimens of each surface treatment group were determined by three SBS test methods: Method 1, the conventional SBS test with direct filling of the mold (Ø 4 mm x 3 mm) with resin cement; Method 2, the conventional SBS test with cementation of prefabricated composite cylinders (Ø 4 mm x 3 mm) using resin cement; Method 3, the microshear bond strength (μ SBS) test with cementation of prefabricated composite cylinders (Ø 0.8 mm x 1 mm) using resin cement. The bond strength data were statistically analyzed using two-way analysis of variance (ANOVA) with factors of SBS test method and surface treatment. One-way ANOVA followed by Dunnett T3 test was performed to compare bond strengths. The coefficient of variation (CV) and the Weibull parameters were used to compare the consistency and reliability of the three test methods. In Experiment II, the performance of universal adhesives containing phosphate monomer as a surface treatment agent for zirconia was evaluated with a test method established through Experiment I and compared to that of Alloy Primer. A conventional single-bottle adhesive (Single Bond 2, 3M ESPE) was used as a negative control. Bond strengths were obtained after 24 h of

water storage and after 10,000 thermocycles between 5°C and 55°C with a 25 s dwell time. The bond strength data were statistically analyzed using one-way ANOVA followed by Tukey's HSD test.

Results

Both SBS test method and surface treatment significantly influenced the SBS values ($p < 0.05$). The AP group showed the highest bond strength regardless of the test methods. Only Method 3 (μ SBS test) revealed a significant difference between the P group and the A group, such that, as the SBS values increased, the CV decreased and the Weibull parameters increased. Method 3 was the most discriminative test method, producing consistent and reliable results. Method 3 was thus used to evaluate the effects of the universal adhesives on the bond strength of resin cement to zirconia. Single Bond Universal showed the highest initial bond strength (37.7 ± 5.1 MPa), followed by All-Bond Universal (31.3 ± 5.6 MPa), Alloy Primer (26.9 ± 5.1 MPa), and Single Bond 2 (8.5 ± 4.6 MPa). Artificial aging significantly reduced the bond strengths of all the test groups ($p < 0.05$). However, the bond strengths of Single Bond Universal (20.7 ± 6.4 MPa) and All-Bond Universal (26.9 ± 6.9 MPa) remained significantly higher than that of Alloy Primer (10.7 ± 4.2 MPa) after thermocycling ($p < 0.05$).

Conclusions

The μ SBS test was more discriminative in differentiating the effects of surface treatments than the conventional SBS tests. The combination of airborne-particle abrasion and a primer containing phosphate monomer was the most effective in improving the bond

strength of resin cement to zirconia. The universal adhesives significantly improved the bond strength and its durability of resin cement to zirconia when compared to Alloy Primer.

Key words: Adhesion, Microshear bond strength, MDP, Surface treatment, Universal adhesive

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Introduction

As patient's demand for esthetic restorations has increased, zirconia ceramics have been frequently used as frameworks for metal-free restorations (1). The development of computer-aided design and manufacturing (CAD/CAM) technology has contributed to the popularity of zirconia ceramics as substitutions for dental metal alloys, which are generally processed by the lost wax technique (2, 3). Zirconia restorations can be cemented with conventional cements such as glass-ionomer cements due to the superior mechanical properties of zirconia (4, 5). However, a wide variety of clinical applications, including partial coverage coronal restorations and Maryland type resin-bonded fixed partial dentures, requires a reliable bond to zirconia (4, 6). In contrast to silica-based ceramics, hydrofluoric acid etching and silanization are not applicable to zirconia because zirconia lacks a glass phase or silica (4, 7-11). Various mechanical and chemical surface treatments have been suggested to improve the bond strength of resin cement to zirconia (7-15). Nonetheless, establishing a reliable bond to zirconia is still a challenge.

The effects of surface treatments for zirconia bonding have been evaluated through bond strength tests in shear (8, 9, 12, 15, 16), tensile (7, 17-19), microshear (20, 21), and microtensile (10, 14, 22) modes. The bond strength tests are based on the application of shear or tensile stresses to the bonded interface until failure occurs. The failure load (N) is divided by the bonded area (mm^2) to give the bond strength in MPa. Direct comparison of the data obtained from different studies is impractical due to the differences in the test

methods including test protocols, specimen geometry, and loading conditions (23-25). Although a superior bond strength in vitro does not ensure a successful clinical result, the bond strength value is a parameter that can predict the performance of a bonding technique or system in the clinical environment (26).

Most studies on zirconia bonding have used shear bond strength (SBS) tests (8, 9, 12, 15, 16). SBS tests conducted in the previous studies can be classified into three types. In the first method (Method 1), a mold, which was positioned on a zirconia specimen, was filled up with luting cement to fabricate a bonded specimen (16). In the second method (Method 2), a prefabricated composite cylinder was cemented to a zirconia specimen using luting cement (8, 9, 12, 15). Both of these two methods used a bonding area of about 4 mm in diameter and were referred to as the conventional SBS tests. The third method (Method 3) was the microshear bond strength (μ SBS) test that used small-diameter tubing of approximately 1 mm as a mold (20, 21). To date, there is no consensus with regard to an appropriate test method for evaluating the bond strength of resin cement to zirconia. Lack of standardization in the SBS testing methods also makes it difficult to compare the results of different studies.

Previous studies have proposed various surface treatments for improving the resin bond to zirconia, such as a vapor phase deposition technique (10), glass micro-pearls (12), selective infiltration etching (14), and plasma spraying (15). However, these techniques require further investigation for clinical application. Although there is no consensus on the most suitable surface treatment for zirconia bonding, the combination of airborne-particle abrasion for micromechanical interlocking and treatment with phosphate

monomer-containing luting agents for chemical bonding has been recommended (7, 8, 19, 27, 28).

Commercially available surface treatment agents for zirconia contain functional monomers, which are typically derived from the reaction of methacrylic acid with phosphoric acid or carboxylic acid (13, 16, 28, 29). One agent, 10-methacryloyloxydecyl dihydrogen phosphate (MDP, Figure 1), has been shown to provide chemical bonds between methacrylate-based composites and zirconia (13, 17, 27, 28, 30). MDP was first introduced by Kuraray Co. (Okayama, Japan) and has been included in the resin cements of PanaviaTM, Alloy Primer, ClearfilTM Ceramic Primer, and ClearfilTM SE Bond. Recently, other manufacturers have introduced new MDP-containing adhesives to the dental market. These MDP-containing adhesives are supplied in a single bottle and called ‘universal’ adhesives because they can be used in etch-and-rinse or self-etch modes on the tooth substrates (31, 32). In addition, the manufacturers have suggested that these adhesives promote the bond between methacrylate-based composites and various indirect restorative materials, including zirconia ceramics and dental non-precious metal alloys, with no need for an additional primer. However, little information available about how these universal adhesives affect the resin bond to zirconia.

The first purpose of this study was to determine the bond strength of resin cement to zirconia ceramic after different surface treatments by means of three SBS test methods and to compare the sensitivity and the reliability of the test methods. The second purpose was to evaluate the performance of the new universal adhesives as a surface treatment agent for zirconia with a test method established through the foregoing experiment.

Experiment I: Comparison of shear test methods to zirconia

Materials and methods

The materials used in this study are shown in Table 1.

Zirconia slab preparation

A total of 120 zirconia ceramic slabs (10 mm x 10 mm x 3 mm) were made from a partially sintered milling block (Cercon[®] base, DeguDent, Hanau, Germany) and then sintered according to the manufacturer's instructions. The fully sintered zirconia specimens were embedded into acrylic resin blocks and sequentially polished with up to 600-grit silicon carbide paper using a polishing machine (Rotapol-V, Struers, Ballerup, Denmark) under water cooling, followed by ultrasonic cleaning in isopropyl alcohol for 3 min. The specimens were randomly divided into four groups of 30 specimens each according to their surface treatments. The group codes for surface treatments and the detailed procedures are summarized in Table 2. The specimens of each surface treatment group were further divided according to the three different SBS test methods ($n = 10$).

Conventional shear bond strength (SBS) test

Bonded specimens for the conventional SBS tests were prepared by two different procedures. In Method 1, a polytetrafluoroethylene (PTFE) mold (4 mm in inner diameter and 3mm in height) was placed on the zirconia slab. Resin cement (Multilink N, Ivoclar Vivadent, Schaan, Liechtenstein) was injected directly into the mold through an automix tip of the resin cement syringe. The cement was light-polymerized from four directions onto the mold for 20 s per side with a light-emitting diode (LED) curing unit (Elipar FreeLight 2, 3M ESPE, St. Paul, MN, USA). The light intensity of 800 mW/cm² was frequently monitored with a radiometer (Demetron 100, Demetron Research Co., Danbury, CT, USA). After 30 min at room temperature, the mold was carefully removed from the bonded specimen.

In Method 2, the same PTFE molds were used to fabricate composite cylinders. The mold was filled with composite resin (Filtek Z-250, Shade A3, 3M ESPE) and it was light-polymerized from four directions for 20 s per side. After polymerization, the composite cylinder was removed from the mold. The composite cylinder was cemented to the zirconia slab using Multilink N resin cement under a fixed load of 10 N (81.2 gf/mm²), which can be considered as a crown seating force (33, 34). Excess resin cement was removed with a microbrush and a dental explorer. After applying an oxygen-inhibiting gel (Liquistrip, Ivoclar Vivadent) around the bonded interface, the cement was light-polymerized from four directions for 20 s per side.

The bonded specimens were stored in distilled water at 37°C for 24 h before testing. Shear bond strengths were measured with a universal testing machine (LF Plus, Lloyd Instruments, Fareham, UK). A mon-angled chisel was placed as close as practically possible to the bonded interface. The shear force was applied at a crosshead speed of 0.5 mm/min until failure occurred.

Microshear bond strength (μ SBS) test

In Method 3, composite resin cylinders (0.8 mm in diameter and 1mm in height) were fabricated by filling polyethylene tubing (Tygon[®] R-3603 tubing, Saint-Gobain Co., Courbevoie, France) with composite resin (Filtek Z-250, Shade A3, 3M ESPE). The composite resin was light-polymerized from four directions for 20 s per side and then removed from the tubing. Multilink N resin cement was applied onto the composite cylinder, which was then placed on the zirconia slab under a fixed load of 0.4 N (81.2 gf/mm²). The luting procedure including light-polymerization was performed in the same manner described in Method 2. The bonded specimens were stored in distilled water at 37°C for 24 h before testing. For measuring bond strengths, a stainless steel orthodontic wire of 0.2 mm in diameter was used to apply a shear force to the bonded interface (Figure 2). The wire, which was attached to the universal testing machine, was looped around the composite cylinder as close as possible to the bonded interface. The shear force was applied at a crosshead speed of 0.5 mm/min until failure occurred.

Analysis of failure mode

The fractured interfaces of the specimens were examined with a stereomicroscope (SZ4045, Olympus Optical Co. Ltd., Tokyo, Japan) at 40× magnification to determine the failure mode. The failure mode was classified as ‘adhesive failure’ when it occurred at the zirconia surface. On the other hand, it was classified as ‘mixed failure’ when adhesive fracture and cohesive fracture within the resin cement occurred simultaneously and as a result the zirconia surface was partly covered by the remaining resin cement. Representative fractured zirconia specimens were examined using a field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi High Technologies Co., Tokyo, Japan) with an acceleration voltage of 15 kV.

Statistical analysis

The bond strength data were analyzed using statistical software (SPSS 18.0, SPSS Inc., Chicago, IL, USA). Two-way analysis of variance (ANOVA), with 1 within-subject factor (surface treatment, 4 levels) and 1 between-subject factor (test method, 3 levels), was used to analyze the effects of the independent factors and the interaction. To interpret the main effects, one-way ANOVA was performed for the surface treatment factor within

each test method, and for the test method factor within each surface treatment. Dunnett T3 test was selected for post hoc pairwise comparisons. The analyses were performed at a significance level of $\alpha = 0.05$.

To compare the reliability of the three test methods, the coefficient of variation (CV) and the Weibull parameters were used. The CV was calculated by dividing the standard deviation by the mean value (24, 25). Using the Weibull distribution of the bond strength values of each test group, the Weibull modulus (m) and the characteristic strength (σ_0) were obtained to compare the three test methods (25, 35, 36). The σ_0 is the stress level at which 63% of the specimens have failed (35, 36).

Results

The means and standard deviations of bond strengths are summarized in Table 3. The two-way ANOVA showed that both SBS test method ($F = 600.1$, $p < 0.001$) and surface treatment ($F = 471.8$, $p < 0.001$) significantly influenced the bond strength values (Table 4). There was also a significant interaction between SBS test method and surface treatment ($F = 145.1$, $p < 0.001$). As shown in Table 3, Method 3 resulted in significantly higher bond strengths than Methods 1 and 2 for each surface treatment ($p < 0.05$). The AP groups showed the highest bond strengths regardless of the test methods. There was no significant difference in mean bond strengths between the P group and the A group in

Methods 1 and 2. In contrast, the P group showed a significantly higher bond strength than the A group in Method 3 ($p < 0.05$).

The distribution of failure modes for each test method is presented in Figure 3. With surface treatments C and A, all of the specimens failed adhesively at the zirconia surface regardless of the test methods. With surface treatment AP, 40%, 30%, and 30% of the specimens were classified as mixed failure with Methods 1, 2, and 3, respectively. Figures 4 and 5 show representative SEM images of the zirconia surface after bond strength tests.

In each test method, the AP group showed the highest σ_0 , followed in order by the P group, the A group, and the C group (Table 5). These results were in line with the distribution of mean bond strengths. For each surface treatment, Methods 2 and 3 presented a lower CV and higher m than Method 1. A lower CV indicates low variability and the consistency of result. In addition, a high m indicates that the flaw population is consistent and a high reliability of σ_0 (35, 36). Methods 2 and 3 were considered more reproducible than Method 1. On the other hand, in contrast to Method 2, Method 3 revealed a significant difference between the P group and A group. Additionally, in Method 2 the AP groups showed a higher CV and lower m than the P groups, although the AP group showed the highest mean SBS and σ_0 . In Method 3, on the contrary, the AP group showed the lowest CV and the highest m , which was in accordance with the highest mean SBS and σ_0 . Method 3 was the most discriminative in evaluating the effect of surface treatments, presenting a high consistency and reliability. Method 3, the μ SBS test, was thus selected to evaluate the effects of the universal adhesives on the bond strength of resin cement to zirconia compared to that of a conventional MDP-containing primer (Alloy Primer).

Experiment II: Shear bond strength of multi-purpose, universal adhesives to zirconia

Materials and methods

One hundred and sixty zirconia slabs and composite cylinders (0.8 mm in diameter and 1mm in height) were prepared in the same manner described in Experiment I. The zirconia surface was sequentially polished with up to 600-grit silicon carbide paper under water cooling and then underwent ultrasonic cleaning in isopropyl alcohol for 3 min. The specimens were randomly divided into four groups of 40 specimens each according to the surface treatment agents: a conventional single-bottle adhesive (Single Bond 2, 3M ESPE), two MDP-containing universal adhesives (Single Bond Universal, 3M ESPE and All-Bond Universal, Bisco Inc., Schaumburg, IL, USA), and a conventional MDP-containing primer (Alloy Primer, Kuraray Co.). The features and main components of the four agents are summarized in Table 1.

The surface treatment agents were applied to the polished zirconia specimens strictly in accordance with the respective manufacturers' instructions. Although Single Bond 2 is not designed for zirconia bonding, it was used as a negative control for the MDP-containing agents. The composite cylinders were cemented to the surface conditioned zirconia specimens with resin cement (RelyX ARC, 3M ESPE) in the same manner as

Method 3 in Experiment I. After 30 min at room temperature, the bonded specimens were stored in distilled water at 37°C for 24 h. Next, 20 specimens of each group were immediately subjected to the bond strength test. The remaining 20 specimens of each group were subjected to thermocycling for 10,000 cycles between 5°C and 55°C with a 25 s dwell time before testing. The microshear bond strength test was performed using the same method and the same universal testing machine used in the Method 3 of the Experiment I.

The fractured interfaces of the specimens were examined with a stereomicroscope (SZ4045, Olympus Optical Co. Ltd.) at 40× magnification to determine the failure mode. The failure mode was classified as ‘adhesive failure’ and ‘mixed failure’ according to the criteria described in Experiment I.

The bond strength data were analyzed using statistical software (SPSS 18.0, SPSS Inc.). One-way analysis of variance (ANOVA), followed by Tukey’s HSD test for post-hoc pairwise comparisons, was performed to assess the differences among the surface treatment agents. For each agent, the effect of thermocycling on the bond strength was investigated using the two-sample *t*-test. The analyses were performed at a significance level of $\alpha = 0.05$.

Results

The mean bond strengths and standard deviations are summarized in Table 6. Single Bond Universal, All-Bond Universal, and Alloy Primer significantly improved the bond strength of resin cement to zirconia when compared to Single Bond 2 ($p < 0.05$). The universal adhesives (Single Bond Universal and All-Bond Universal) showed significantly higher bond strengths than the conventional MDP-containing primer (Alloy Primer) regardless of the storage condition ($p < 0.05$).

Before thermocycling, Single Bond Universal showed the highest bond strength ($p < 0.05$). The bond strengths for all of the treatment agents were significantly reduced after thermocycling ($p < 0.05$). All-Bond Universal showed a significantly higher bond strength than Single Bond Universal after thermocycling ($p < 0.05$).

The distribution of failure modes after the bond strength test is presented in Figure 6. Regardless of the storage condition, all of the specimens for Single Bond 2 were classified as adhesive failure after fracture. With the three MDP-containing agents, mixed failures (60–95%) predominated before thermocycling, but adhesive failures (60–90%) occurred more frequently than mixed failures (10–40%) after thermocycling.

Discussion

This study compared the sensitivity and the reliability of three SBS test methods. The μ SBS test presented the highest sensitivity and reliability among three SBS test methods, and thus was selected to evaluate the performance of universal adhesives (Single Bond Universal and All-bond Universal) as a surface treatment agent for promoting zirconia bonding. The universal adhesives showed significantly higher bond strengths compared to a conventional MDP-containing primer (Alloy Primer).

Various surface treatment methods have been suggested to improve bond strength of resin-based materials to zirconia and have been evaluated through bond strength tests (7-22). SBS tests have been widely used in the studies on zirconia bonding due to the ease of specimen preparation and simplicity of the test protocol (8, 9, 12, 15, 16). SBS tests more closely simulate the clinical situation compared to tensile bond strength tests (37). On the other hand, SBS tests have been criticized for non-homogeneous stress distributions at the bonded interface, inducing cohesive failures within the base substrates and a misinterpretation of results (23, 38, 39). However, cohesive failures within zirconia have rarely been reported due to the superior mechanical properties of the material (8, 9).

In Experiment I, SBS tests were classified into three types and their sensitivity and reliability were compared with each other. Both SBS test method and surface treatment influenced the bond strength values. Method 2 presented significantly higher bond strengths than Method 1 for surface treatments C and A. The bonded areas in Methods 1

and 2 were identical. However, the resin cement was passively applied on the zirconia specimen in Method 1, whereas it was under even pressure during the luting procedure in Method 2. The pressure may have promoted the adaptation of the resin cement to the zirconia ceramic, resulting in higher bond strengths in Method 2 (40). The difference in the results of the two methods can also be attributed to the thickness of the resin cement. The entire mold was filled with resin cement in Method 1, whereas in Method 2, it formed a layer between the composite cylinder and the zirconia slab. The thickness of the resin cement can be considered infinite in Method 1. The excessive thickness of a luting agent has an unfavorable influence on the bond strength between a restoration and the substrate due to its inferior mechanical properties and high polymerization shrinkage (41). SBS test with luting procedure is considered to be more relevant to the clinical situation in which resin cement exists in a thin layer between a restoration and tooth substrate.

Method 1 presented higher CV and lower m values than Methods 2 and 3 for each surface treatment. The passive application of resin cement in Method 1 may have caused uneven adaptation of the resin cement to the zirconia specimen, thus resulting in relatively high variations as well as lower bond strength values. In addition, luting the prefabricated composite cylinders with resin cement was easier to control than filling the entire mold with resin cement. This may have contributed to the more consistent results obtained from Methods 2 and 3.

Method 3, the μ SBS test, resulted in significantly higher bond strengths than Methods 1 and 2 for each surface treatment. The main characteristic of the μ SBS test is the testing of a smaller area compared to the conventional SBS test. According to a study on

microtensile bond strength (μ TBS) test (42), the bond strength was inversely related to the bonded area. Brittle materials, such as ceramics and composite resins, fail due to the propagation of existing flaws when subjected to stresses above a critical level (43). The small bonded area contains fewer defects and thus results in a higher bond strength value. This principle also explains why Method 3 resulted in higher bond strengths than Methods 1 and 2.

In the Weibull statistics, a high m indicates that the flaw population is consistent and the bonding procedure is reliable (35, 36). If the flaw population is consistent in the specimens within a group, m (reliability) will increase with the increase of σ_0 (probability of failure for a given stress level), reflecting a relative decrease in the variation within the group, that is, low variability and low spread in bond strength with high reliability of σ_0 . The scales of the Weibull parameters are wider than those of the CV and mean values, and thus the parameters are more discernible (36). Therefore, in addition to the CV and mean values, both of the Weibull parameters m and σ_0 should be considered in evaluating the consistency and reliability of the test methods. In the present study, Methods 2 and 3 were similar in CV values. However, comparing the CV and m of the four surface treatment groups, Method 3 showed the lowest CV with the highest mean bond strength in accordance with the highest m and σ_0 . In addition, only Method 3 revealed a significant difference between the P group and the A group. Method 3 was thus considered the most discriminative and reliable test method in terms of the consistency of specimens. This assumption is supported by previous studies conducted on enamel, where the μ SBS test showed advantages in differentiating the performance of dental adhesive systems and providing consistent results without the premature failures that frequently occurred in the

μ TBS test (44, 45). Shimada and his research group (46-48) have reported that the μ SBS test maximizes shear forces at the bonded interface and gives precise results with relatively small standard deviations. Another advantage of the μ SBS test is that a small testing area allows the regional mapping and many tests to be performed on the same substrate.

The criticisms for SBS tests are related to a high prevalence of cohesive failures within the base substrates (23, 38, 39). However, this contention has been based on the studies using dentin or glass-ceramics that have relatively lower cohesive strengths. Cohesive failures within zirconia were not observed in the present study, which was in accordance with previous studies on zirconia bonding (8, 9). There was no microscopic alteration of the zirconia surface after adhesive failures, which implied that the bonded interface between the resin cement and zirconia ceramic was the weakest link (Figure 4). In contrast, mixed failures, in which the zirconia surface was partly covered by the remaining resin cement, were associated with a higher bond strength. In Experiment I, the AP groups presented an average of 33% mixed failure in accordance with their highest mean SBS. In Experiment II, the specimens for the MDP-containing agents presented primarily mixed failures before thermocycling, whereas there was an increase in adhesive failures coupled with the reduced bond strengths after thermocycling. When SBS tests are conducted on zirconia ceramics, the concerns related to cohesive failures within weak substrates such as dentin are reduced.

Although the present study was focused on the SBS tests, the μ TBS tests have been widely used to evaluate the bond to tooth substrates and also to evaluate the bond strength

of resin cement to zirconia in some studies (10, 14, 22). The μ TBS tests allow for a more homogeneous distribution of stress and evaluation of the bond strength of a small region of interest within the substrates. However, premature failures frequently occur during the fabrication procedures of the μ TBS test specimens. Cutting the specimens into microbeams is a technically sensitive and labor-intensive step. The cutting procedure can also cause microcracks in brittle materials like ceramics (49). It is very difficult to cut zirconia into microbeams without damaging the specimens because of the superior mechanical properties of the material. A previous study (50), in which the μ TBS test was compared with the conventional SBS test, showed that the test method did not significantly affect the bond strength results of resin cement to glass-infiltrated alumina-zirconia ceramic. In Experiment I, the μ SBS test allowed for the differentiation between the effects of surface treatments with low standard deviations through relatively simple procedure. The μ SBS test is considered to be appropriate for screening the performance of surface treatments for improving the resin bond to zirconia.

Although zirconia restorations can be cemented with conventional cements, a reliable bond to zirconia is required in some clinical case such as compromised retention and minimally invasive treatment (4-6). Various surface treatments, including a vapor phase deposition technique (10) , glass micro-pearls (12), selective infiltration etching (14), and plasma spraying (15), have been proven effective in improve the resin bond to zirconia. However, these techniques require the improvement of equipment and simplification of processes for practical use in clinical environments. Another approach to modify the zirconia surface is tribochemical silica coating. It has been widely used to produce a silica layer on non-silica based materials and allows silane coupling agents to be employed (51).

Some studies have showed favorable results on initial bond strength to silica-coated zirconia but the bond strength was significantly reduced after artificial aging (7, 27, 52). It has been assumed that tribochemical silica coating may not produce a uniform silica layer firmly attached to the zirconia surface. The siloxane bond is vulnerable to hydrolytic degradation (51). In contrast, the combination of airborne-particle abrasion and resin cement/primer containing MDP has been shown to provide a long-term durable bond to zirconia (7, 8, 19, 27, 28).

MDP chemically bonds to non-precious metals (53) as well as the tooth substrates (54, 55). MDP has an amphiphilic structure, with the vinyl group as the hydrophobic moiety and the phosphate group as the hydrophilic moiety. The vinyl group can copolymerize with the resin monomer of the resin-based materials applied later. The mechanism for MDP to improve the resin bond to zirconia is assumed that the hydroxyl groups of the phosphate moiety in MDP interact with the hydroxyl groups on the zirconia surface through Van der Waals forces or hydrogen bonds (13). Chen et al. (30) verified the formation of a chemical bond between phosphate monomer and zirconia using time-of-flight secondary ion mass spectroscopy. In Experiment II, the universal adhesives that contain MDP showed significantly higher bond strengths than Single Bond 2. According to the manufacturer, Single Bond Universal differs from Single Bond 2 primarily in the addition of MDP and silane. There was a need to differentiate between the effects of conventional adhesive formulation and MDP on bond strength. For this, Single Bond 2 served as the negative control for the universal adhesives. The higher bond strengths with universal adhesives can be explained by the addition of MDP to conventional adhesive formulations. It has been proven that MDP is effective in improving bond strength of

resin-based materials to zirconia through extensive research including this study. However, more research is needed to disclose possible interactions between MDP and other compositions mixed into a single-bottle solution and to determine the precise molecular mechanism of the interactions between MDP and the zirconia surface.

Single Bond Universal showed the highest initial bond strength but showed a significantly lower bond strength than All-Bond Universal after thermocycling. In contrast to All-Bond Universal, Single Bond Universal contains a silane in addition to MDP. The silane could contribute to improving the initial bond strength by increasing the wettability of the zirconia surface (13), although the silane cannot chemically bond to zirconia due to the lack of silica in zirconia. However, it seems that the silane increases the hydrophilicity of Single Bond Universal, thereby predisposing the adhesive layer to hydrolytic degradation (51, 56).

Single Bond Universal and All-Bond Universal showed significantly higher bond strengths than Alloy Primer, a conventional MDP-containing primer. Although Alloy Primer was originally designed to enhance the bond between resin-based materials and dental metal alloys, it has provided a superior bond to zirconia compared to other phosphate monomer-containing primers (16, 18, 19). In contrast to Alloy Primer, the universal adhesives have resin adhesive components, which could allow the resin cement to flow more easily and strengthen the interfacial layer through copolymerizing with the resin cement. Separate surface treatment agents for zirconia, such as Alloy Primer, can be substituted with the universal adhesives. The universal adhesives have also shown comparable performance on the tooth substrates compared to conventional adhesives (31,

32). The clinical procedure of cementing zirconia restorations will be simpler and more efficient with the single-bottle, universal adhesives.

In Experiment I, the AP group exhibited the highest bond strengths in accordance with previous studies (7, 8, 19, 27, 28). Airborne-particle abrasion increases the surface roughness, thereby improving micromechanical retention to zirconia ceramics. The phosphate monomer, such as MDP, produces a chemical bond between resin cement and zirconia ceramic (4). On the other hand, there are controversial results about which of mechanical or chemical treatments is a stronger contributing factor for zirconia bonding (16, 19, 21). The P group exhibited significantly higher bond strength than the A group in Method 3, which was more sensitive to the effects of surface treatments. Based on this finding, the resin bond to zirconia may rely mainly on chemical bonds rather than micromechanical retention. This assumption is supported by previous studies that showed no correlation between surface roughness and bond strength (19, 28, 57). Large-size particles at a high blasting pressure increased surface roughness but it did not result in a higher bond strength of resin cement to zirconia (28, 57). Another argument is that airborne-particle abrasion can induce phase transition and produce microcracks within the zirconia surface, which influence the mechanical properties of zirconia (58, 59). Özcan et al. (58) reported that air abrasion with 50 μm Al_2O_3 particles at 2.8 bar pressure decreased the biaxial flexural strength of the zirconia.

In Experiment II, the polished zirconia specimens were used without airborne-particle abrasion in order to focus on the role of surface treatment agents. However, previous long-term studies have shown that the chemical bonds are not water-resistant (2, 10, 11,

13, 17), and the present study also showed that bond strengths to chemically treated zirconia using the surface treatment agents significantly decreased after thermocycling. Airborne-particle abrasion, which has a surface activation and cleaning effect, is required to promote chemical bonds and to increase the bond durability (19). Airborne-particle abrasion with silica coated Al_2O_3 particles at reduced pressure has been recommended for producing a durable bond to zirconia with minimal influence on the mechanical properties of the material (22, 58, 59). Airborne-particle abrasion, combined with the universal adhesives, is expected to increase the durability of zirconia bonding and further investigations should be conducted with various airborne-particle abrasion protocols.

Conclusions

Within the limitations of the present study, the SBS test methods with luting procedure, in which prefabricated composite cylinders were cemented to zirconia using resin cement, were more reliable and reproducible for evaluating the bond strength of resin cement to zirconia. The μ SBS test was more discriminative in evaluating the effects of surface treatments than the conventional SBS tests. Although it seems that the resin bond to zirconia relies mainly on chemical bonds, the combination of airborne-particle abrasion and MDP-containing primers is recommended for improving the bond strength of resin cement to zirconia. The universal adhesives containing MDP functional monomer showed better performance in terms of the bond strength of resin cement to zirconia compared to Alloy Primer, a conventional MDP-containing primer. The universal adhesives could make the clinical procedure of cementing zirconia restorations simpler and more efficient.

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Tables and Figures

Table 1. Materials used in this study

Material	Feature	Composition	Manufacturer	Batch no.
Cercon[®] base	Zirconia blank	Zirconium oxide, yttrium trioxide, hafnium dioxide	DeguDent, Hanau, Germany	18009687
Alloy Primer	Conventional MDP-containing primer	VBATDT, MDP, acetone	Kuraray Co., Osaka, Japan	00442B
Single Bond Universal	Single-bottle MDP-containing adhesive	MDP, bis-GMA, HEMA, DMA, methacrylate functional copolymer, filler, ethanol, water, initiators, silane	3M ESPE, St. Paul, MN, USA	502225
All-bond Universal	Single-bottle MDP-containing adhesive	MDP, bis-GMA, HEMA, ethanol, water, initiators	Bisco Inc., Schaumburg, IL, USA	1200013674
Single Bond 2	Conventional single-bottle adhesive	bis-GMA, HEMA, DMA, methacrylate functional copolymer, filler, ethanol, water, photoinitiator	3M ESPE, St. Paul, MN, USA	N412273
Multilink N	Resin cement	DMA, HEMA, barium glass, ytterbium trifluoride, spheroid mixed oxide	Ivoclar Vivadent, Schaan, Liechtenstein	R86339
RelyX ARC	Resin cement	bis-GMA, TEG-DMA, zirconia/silica filler, DMA, amine, photoinitiator, BP, pigment	3M ESPE, St. Paul, MN, USA	N441122

(continued)

Abbreviations: MDP, 10-methacryloyloxydecyl dihydrogen phosphate; VBATDT, 6-(4-vinylbenzyl-n-propyl amino)-1,3,5-triazine-2,4-dithione; bis-GMA, bisphenol A diglycidyl ethermethacrylate; HEMA, hydroxyethyl methacrylate; DMA, dimethacrylate; TEG-DMA, triethylene glycol dimethacrylate; BP, benzoyl peroxide.

Table 2. Surface treatment group codes and the corresponding procedures for zirconia

Group	Surface treatment procedure
C	No further treatment (control)
A	Airborne-particle abrasion with 50 μm aluminum-oxide (Al_2O_3) particles at 0.28 MPa for 20 s at a distance of 10 mm, followed by ultrasonic cleaning in isopropyl alcohol for 3 min
P	Treatment with Alloy Primer according to the manufacturer's instructions
AP	Treatment with Alloy Primer after airborne-particle abrasion

Table 3. The mean shear bond strengths (in MPa) after four different surface treatments measured with three different shear bond strength test methods

Surface treatment	Shear bond strength test method		
	Method 1	Method 2	Method 3
C	0.5 (0.2) ^A _a	1.3 (0.4) ^A _b	2.3 (0.5) ^A _c
A	3.5 (0.7) ^B _a	4.7 (0.7) ^B _b	5.9 (1.0) ^B _c
P	4.5 (0.7) ^B _a	4.9 (0.6) ^B _a	24.6 (3.5) ^C _b
AP	8.1 (1.6) ^C _a	9.8 (1.4) ^C _a	29.7 (3.5) ^D _b

The numbers in the parentheses are standard deviations.

Different superscript uppercase letters indicate significant differences between mean values within the same column ($p < 0.05$). Different subscript lowercase letters indicate significant differences between mean values within the same row ($p < 0.05$).

Group codes: C, control; A, airborne-particle abrasion; P, treatment with Alloy Primer; Method 1, the conventional shear bond strength test with direct filling of the mold with resin cement; Method 2, the conventional shear bond strength test with cementation of the prefabricated composite cylinder using resin cement; Method 3, the microshear bond strength test with cementation of the prefabricated composite cylinder using resin cement.

Table 4. Two-way ANOVA results of bond strength data after four different surface treatments measured with three different shear bond strength test methods

Source	Sum of squares	df	Mean squares	F	p value
Surface treatment	3818.0	3	1272.7	471.8	< 0.001
Test method	3237.8	2	1618.9	600.1	< 0.001
Between	2348.3	6	391.4	145.1	< 0.001
Error	291.4	108	2.7		
Total	18020.5	120			

Table 5. Coefficient of variation (CV), Weibull modulus (m), and characteristic strength (σ_0 in MPa) of the shear bond strength values of four different surface treatment groups measured with three different shear bond strength test methods

Surface treatment	Shear bond strength test method								
	Method 1			Method 2			Method 3		
	CV	m	σ_0	CV	m	σ_0	CV	m	σ_0
C	0.40	2.89	0.59	0.26	4.38	1.47	0.22	5.26	2.53
A	0.21	5.59	3.81	0.15	8.19	4.95	0.16	7.10	6.32
P	0.16	6.99	4.76	0.12	9.91	5.19	0.14	8.22	26.07
AP	0.20	5.59	8.74	0.14	7.95	10.44	0.12	10.07	31.21

Group codes: C, control; A, airborne-particle abrasion; P, treatment with Alloy Primer; Method 1, the conventional shear bond strength test with direct filling of the mold with resin cement; Method 2, the conventional shear bond strength test with cementation of the prefabricated composite cylinder using resin cement; Method 3, the microshear bond strength test with cementation of the prefabricated composite cylinder using resin cement.

Table 6. Means of microshear bond strength (in MPa) of resin cement to zirconia ceramic with different surface treatment agents

Surface treatment agent	24 h	10,000 thermocycling
Single Bond 2	8.5 (4.6) ^D _a	0.3 (0.1) ^D _b
Single Bond Universal	37.7 (5.1) ^A _a	20.7 (6.4) ^B _b
All-Bond Universal	31.3 (5.6) ^B _a	26.9 (6.4) ^A _b
Alloy Primer	26.9 (5.1) ^C _a	10.7 (4.2) ^C _b

The numbers in the parentheses are standard deviations.

Different superscript uppercase letters indicate significant differences between mean values within the same column ($p < 0.05$). Different subscript lowercase letters indicate significant differences between mean values within the same row ($p < 0.05$).

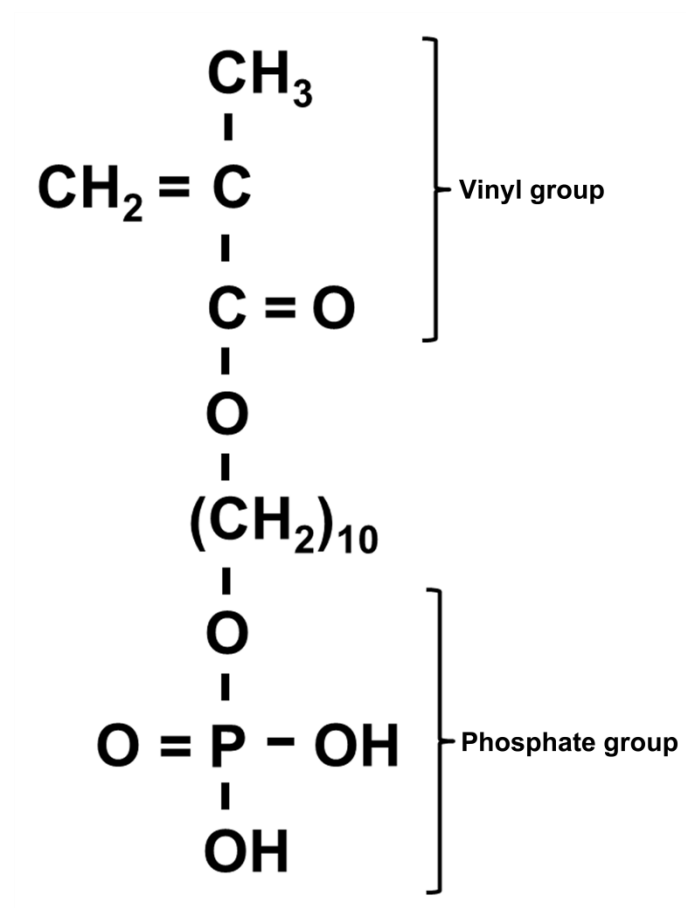


Figure 1. Amphiphilic structure of the MDP monomer.

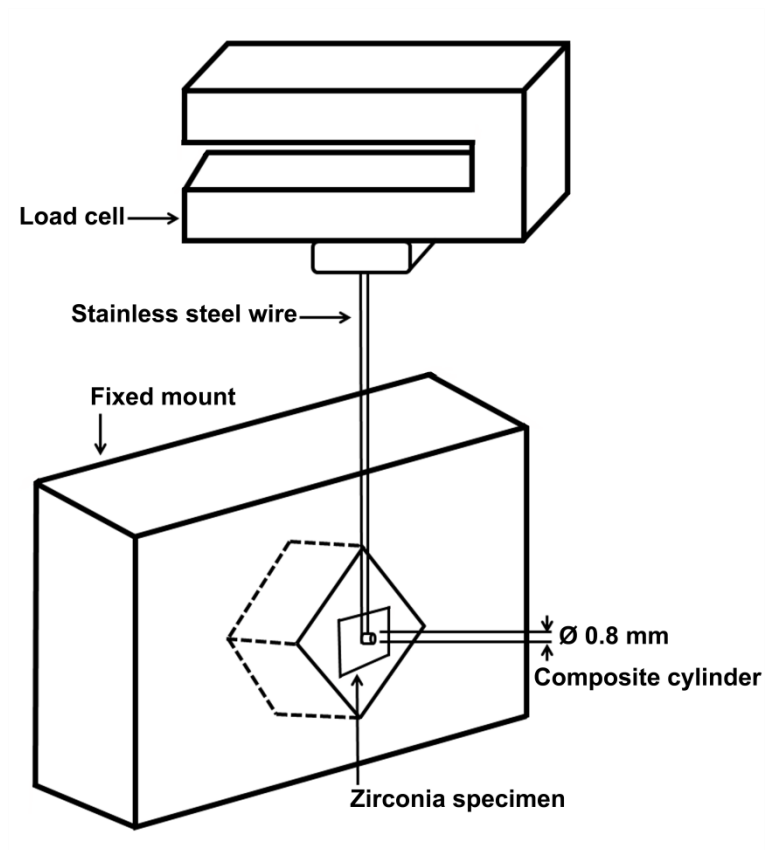


Figure 2. Schematic drawing of the microshear bond strength test.

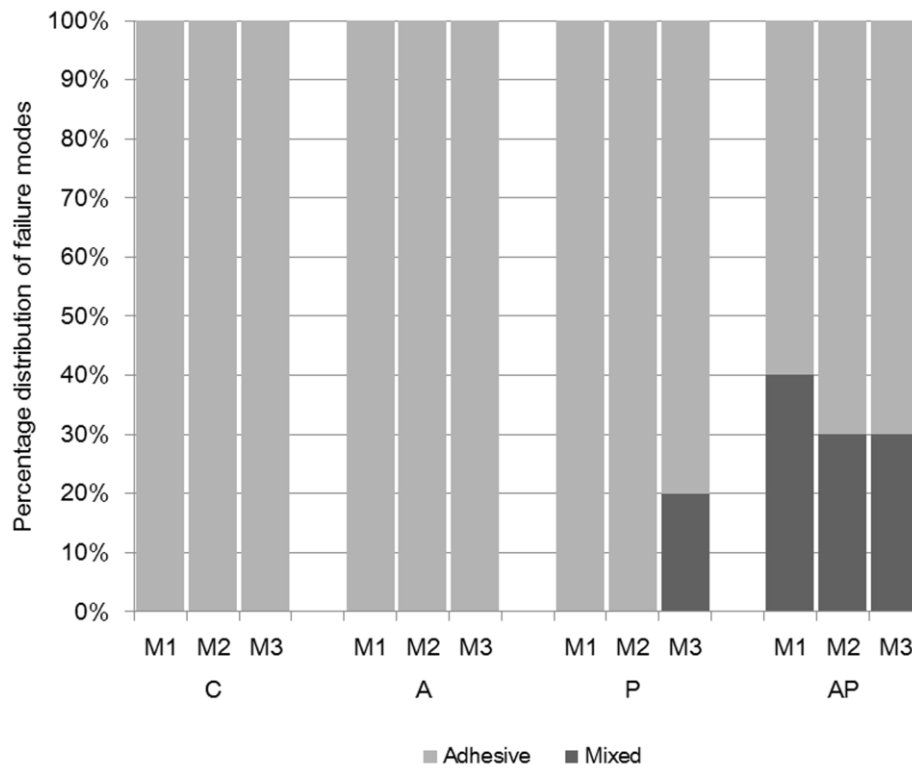


Figure 3. Failure mode distribution after three different shear bond strength tests.

Group codes: C, control; A, airborne-particle abrasion; P, treatment with Alloy Primer; M1, the conventional shear bond strength test with direct filling of the mold with resin cement; M2, the conventional shear bond strength test with cementation of the prefabricated composite cylinder using resin cement; M3, the microshear bond strength test with cementation of the prefabricated composite cylinder using resin cement.

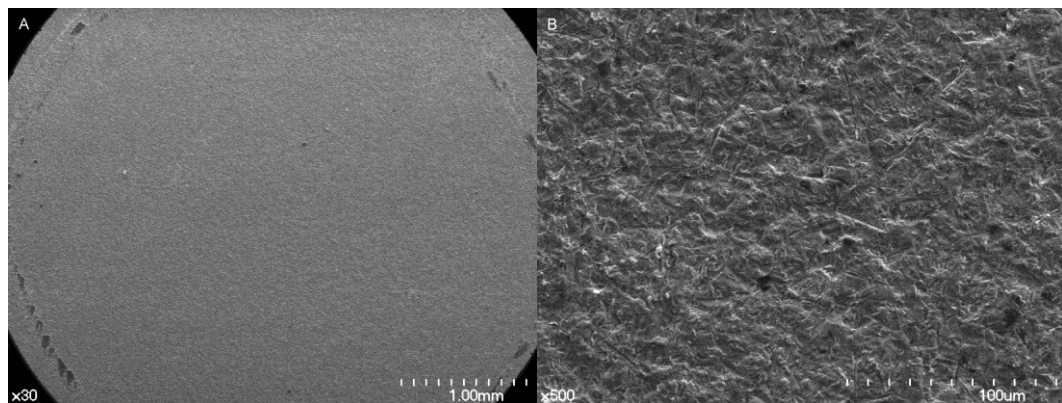


Figure 4. Representative scanning electron microscopic image of adhesive failure. This specimen was selected from the A group tested with Method 1. (A) The zirconia surface was exposed without any resin cement remnants after fracture. (B) The high magnification image of the specimen showing the typical topography of air-abraded zirconia after adhesive failure.

Group codes: A, airborne-particle abrasion; Method 1, the conventional shear bond strength test with direct filling of the mold with resin cement.

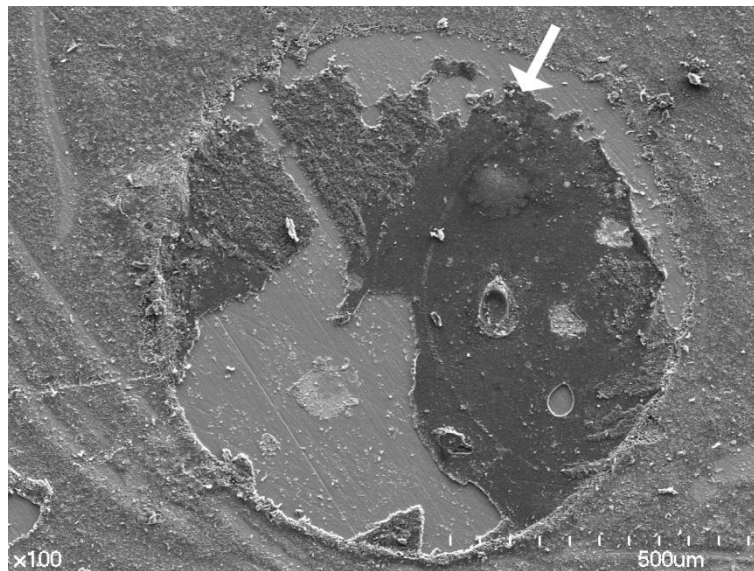


Figure 5. Representative scanning electron microscopic image of mixed failure. This specimen was selected from the P group tested with Method 3. The arrow shows the direction of shear force. The resin cement remained on the side of the loading point. At the opposite side of loading, the fracture did not propagate into the zirconia substrate because of its superior mechanical properties.

Group codes: P, treatment with Alloy Primer; Method 3, the microshear bond strength test with cementation of the prefabricated composite cylinder using resin cement.

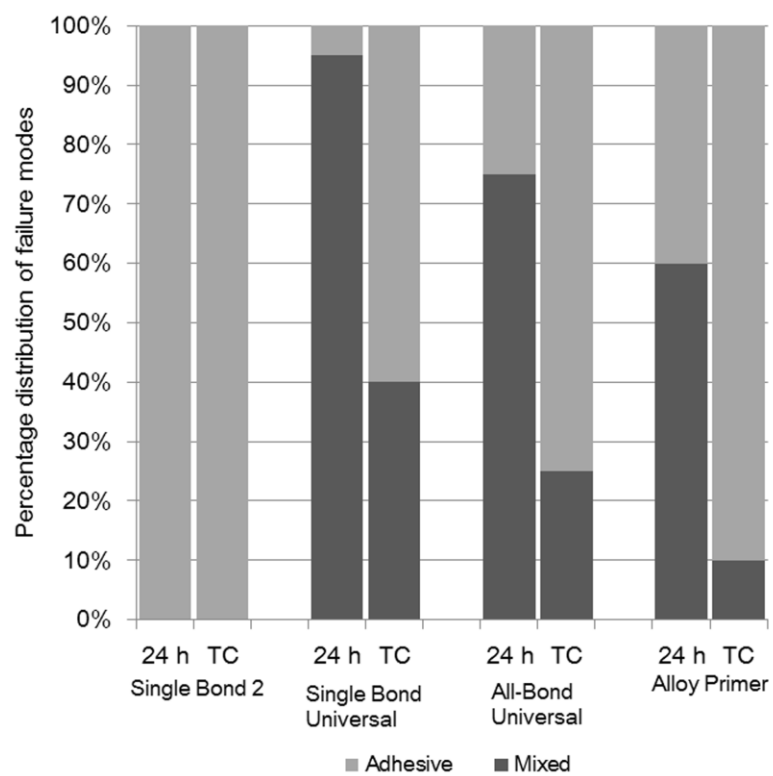


Figure 6. Failure mode distribution after 24 h of water storage and 10,000 cycles of thermocycling.

치과용 지르코니아 세라믹에 대한 접착

I. 지르코니아에 대한 전단접착강도 시험방법의 비교

II. 범용 Universal adhesives의 지르코니아에 대한 전단접착강도

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목적

다양한 전단접착강도 시험방법을 통해 측정된 지르코니아 세라믹에 대한 레진 시멘트의 접착강도를 비교함으로써 지르코니아 표면처리의 효과를 평가하기에 적합한 전단접착강도 시험방법을 확립하고자 하였다. 또한 확립된 전단접착강도 시험방법을 이용해 phosphate functional monomer를 함유하는 최근 출시된 Universal adhesives (Single Bond Universal, 3M ESPE사; All-Bond Universal, Bisco사)의 지르코니아 표면 전처리제로서의 성능을 평가함으로써, 지르코니아

세라믹에 대한 레진 접착을 효율적으로 향상시킬 수 있는 방법을 모색하고자 하였다.

재료 및 방법

지르코니아 세라믹을 slab 형태의 시편으로 제작 후 표면처리방법에 따라 다음과 같이 4개의 군으로 나누었다: C, no treatment; A, airborne-particle abrasion; P, phosphate functional monomer를 함유한 전통적인 표면 전처리제 (Alloy Primer, Kuraray사)를 적용; AP, airborne-particle abrasion된 지르코니아 표면에 Alloy Primer를 적용. 각 실험군에 따라 표면처리된 지르코니아 시편에 대한 레진 시멘트의 접착강도를 다음과 같은 3가지 방법을 통해 제작된 접착시편을 이용해 측정하였다: Method 1, 지르코니아 시편에 직경 4 mm의 원형 mold를 고정하고 혼합된 레진 시멘트를 직접 mold에 주입; Method 2, 직경 4 mm의 원형 mold를 이용해 미리 제작된 복합레진 실린더를 지르코니아 시편에 레진 시멘트를 이용해 접착; Method 3, 직경 0.8 mm의 원형 mold를 이용해 미리 제작된 복합레진 실린더를 지르코니아 시편에 레진 시멘트를 이용해 접착. Method 1과 Method 2는 전통적인 전단접착강도 시험에 해당되고, Method 3는 미세전단접착강도 시험에 해당된다. 전단접착강도 시험방법과 표면처리방법이 접착강도 결과에 미치는 영향을 알아보기 위해 이원배치 분산분석을 시행하였다. 일원배치 분산분석과 Dunnett T3 test를 이용해 실험군에 따른 전단접착강도를 비교하

였다. 변동계수 (coefficient of variation, CV)와 Weibull parameters를 이용해 전단 접착강도 시험방법의 일관성과 신뢰도를 평가하였다. 이를 통해 확립된 전단 접착강도 시험방법을 이용해 2종의 Universal adhesive가 지르코니아에 대한 접착에 미치는 영향을 측정하고 Alloy Primer와 비교하였다. 음성 대조군으로는 phosphate functional monomer를 함유하지 않는 adhesive인 Single Bond 2 (3M ESPE사)를 사용하였으며, 초기접착강도와 5°C 와 55°C 에서 25초씩 1만 회의 열순환 처리 후 접착강도를 측정하였다. 표면 전처리제에 따른 접착강도를 비교하기 위해 일원배치 분산분석 후 Tukey's HSD test를 시행하였다.

결과

전단접착강도 시험방법과 표면처리방법 모두 지르코니아에 대한 레진 시멘트의 접착강도에 유의한 영향을 미쳤다 ($p < 0.05$). 표면처리방법에 있어서는 전단접착강도 시험방법에 상관없이 AP 군이 가장 높은 접착강도를 나타내었다. Method 1과 Method 2에서는 P 군과 A 군 사이에 유의한 차이가 발견되지 않았으나, Method 3에서는 P 군이 A 군 보다 유의하게 높은 접착강도를 나타내었다 ($p < 0.05$). CV와 Weibull parameters를 비교한 결과, Method 1에 비해 Method 2와 Method 3가 균일한 측정결과를 나타내었다. 높은 민감도와 신뢰도를 보인 Method 3를 이용해 Universal adhesives의 지르코니아 표면 전처리제로서의 성능을 평가하였다. Single Bond Universal 군 (37.7 ± 5.1 MPa), All-Bond Universal 군

(31.3 ± 5.6 MPa) 모두 Alloy Primer 군 (26.9 ± 5.1 MPa)과 Single Bond 2 군 (8.5 ± 4.6 MPa)에 비해 유의하게 높은 초기접착강도를 나타내었다 ($p < 0.05$). 열순환 처리 후에 모든 군의 접착강도가 유의하게 감소하였으나 ($p < 0.05$), Single Bond Universal 군 (20.7 ± 6.4 MPa)과 All-bond Universal 군 (26.9 ± 6.4 MPa)은 Alloy Primer 군 (10.7 ± 4.2 MPa)에 비해 유의하게 높은 접착강도를 유지하였다 ($p < 0.05$).

결론

미세전단접착강도 시험은 전통적인 전단접착강도 시험에 비해 민감하였고 균일한 측정결과를 나타내었다. Airborne-particle abrasion 후에 phosphate functional monomer를 함유한 표면 전처리제의 적용이 레진 시멘트의 지르코니아에 대한 접착강도를 가장 효과적으로 증진시켰다. Universal adhesives는 전통적인 표면 전처리제인 Alloy Primer에 비해 레진 시멘트의 지르코니아에 대한 접착강도 및 접착내구성 증진에 보다 효과적이었다.

주요어: 접착, 미세전단접착강도, MDP, 표면처리, Universal adhesive

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